# THE MOLECULAR DISSOCIATION OF VINYLACETYLENE
AND ITS IMPLICATIONS FOR ACETYLENE PYROLYSIS

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Perhaps the most extensively investigated of all fuel pyrolyses is that of acetylene. The reasons are compelling: acetylene is a major product of virtually all hydrocarbon pyrolysis and oxidation, and its reactions usually govern the later states of such processes, in particular the formation of soot. Acetylene is evidently essential to soot formation (1,2), and has also been selected as the prototype fuel in a recent detailed model of the soot formation process (3).

Although C_2H_2 pyrolysis has been observed over an enormous range of temperature (700-3500K) (4-17), and by many different and usually reliable methods, there is little agreement even on its initiation. The process looks much like a single second-order reaction over 700-2500K (5,7) and the early products are commonly dominated by multiples of the C_2H_2 unit. In particular, there is good evidence that vinylacetylene (C_4H_4, 1-buten-3-yne) is the sole initial gaseous product below 1500K (4-8). This all suggests C_2H_2 pyrolysis is largely a molecular polymerization, but the reaction also shows induction periods (11,15), a sensitivity to NO (15), rapid isotopic scrambling in $C_2H_2-C_2D_2$ mixtures (6), as well as minor products suggestive of radical intermediates (6,9,14). All this of course implies chain reaction, and most recent workers (7,9,10,12,17) have described this pyrolysis as an H-atom chain initiated by

$$2C_2H_2 \rightarrow C_4H_3 + H \qquad 1)$$
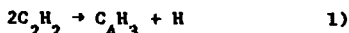
There are also some interesting attempts to reconcile the evidence for chain and molecular reaction which postulate an intermediate triplet C_2H_2 (1,2-diradical) (5,7,18).

Given the effort expended on C_2H_2 pyrolysis the lack of consensus is striking. Much of this must simply reflect the complexity of the process. As noted by Palmer and Dormish (7), it is quite unlikely the same mechanism applies for all conditions. Certainly at very high temperatures, above 2500K, the reaction is a degenerate branched chain (10) which is probably initiated by simple dissociation. In the flow and static reactor studies below 1000K there is obviously a large heterogeneous component (5,7). At the lower temperatures impurities could readily compete as a source of chain initiation.

Some of the above complications may be avoided by observing the reverse process, which could well be the dissociation of vinylacetylene. Decomposition of C_4H_4 has recently been studied in the shock tube by Colket (9) and Hidaka et al. (19). They again suggest a radical chain mechanism initiated by

$$C_4H_4 \rightarrow C_4H_3 + H \qquad 2)$$
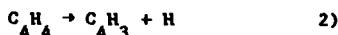
although they derive activation energies for this of 80-85 kcal/mol, which do seem low. The dominant products are C_4H_2 and C_2H_2 with a very consistent C_2H_2/C_4H_2 ratio of 5-10.

In a collaboration with R. D. Kern (20) we have reinvestigated the C_4H_4 decomposition at very high temperatures (1500-2500K) where the unimolecular dissociation should dominate, using laser-schlieren (LS) and

time-of-flight (TOF) mass spectroscopy techniques on shock waves. Here we present a brief reiteration of the C_4H_4 results together with their implications for the C_2H_2 pyrolysis, implications which have led to the proposal of a new mechanism for this reaction.

EXPERIMENTAL

Both the LS (2 and 4% C_4H_4 - Kr, 1650-2500K, 110-427 torr) and TOF (2% C_4H_4 - Ne, 1500-2200K, 150-300 torr) measurements used apparatus and procedures which have been fully described (21,22). Vinylacetylene was obtained from Wiley Organics, degassed and distilled for purification, finally showing no more than ~0.1% impurities. Thermodynamic properties of C_4H_4 were calculated from molecular properties (23), using an estimated $\Delta H_{f,298}^{o}$ = 69 kcal/mol (24). A more detailed description of the experiments and calculations will be found in ref. (20).
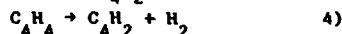
RESULTS

Example LS semilog density gradient profiles are presented in Figure 1. The important feature here is the upward concave shape. This concavity is consistent throughout the LS experiments and shows there can be no significant chain reaction in C_4H_4 pyrolysis. A chain will accelerate the endothermic decomposition producing a convex profile. For example, in benzene (25) and pyridine (26), which evidently dissociate by C-H scission, this acceleration is so severe it generates a local maximum. The likely consequences of such a chain in C_4H_4 are shown in Figure 2 where we have modeled one LS experiment with a "reasonable" chain mechanism, initiated by reaction 1) (see ref. (20) for details). As expected, the result is a strongly convex profile in complete disagreement with the measurements. In fact, even a small contribution from such a chain is excluded. In Figure 2 we also show the sensitivity to small amounts of chain reaction. Even 1% dissociation through reaction 1) produces noticeable deviation.

The TOF profiles also argue against a chain initiated by reaction 1). They show C_2H_2 and C_4H_2 as major products with C_2H_2/C_4H_2 ~5 independent of temperature (or even time) in essential agreement with the other recent shock tube studies (9,19). The problem is any chain initiated by 1) cannot maintain the required dominance of C_2H_2 at high temperatures where the products mainly arise from dissociation (and abstraction). Such a chain then produces the great excess of C_4H_2 shown in Figure 3.

The product distribution and the absence of discernable chain reaction suggest the main channel for C_4H_4 dissociation must be

$$C_4H_4 \rightarrow 2C_2H_2 \qquad \qquad 3)$$
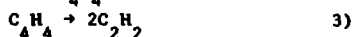
With almost no chain much of the C_4H_2 product must be formed through

$$C_4H_4 \rightarrow C_4H_2 + H_2 \qquad \qquad 4)$$

We have modeled the LS and TOF data using just these two reactions with the uniformly excellent results exemplified in Figures 1,2, and 4. Rate constants for the sum of reactions 3) and 4) (both have ΔH_{298}^{o} very near 40 kcal/mol), derived from the zero-time density gradients, are shown in Figure 5. Here we also show a "routine" RRKM model fit to these data. This model
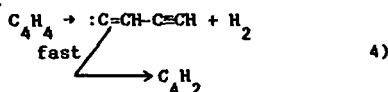
projects an effective barrier of 79.5 $\pm$ 3 kcal/mol and an activation energy for k_∞ of 82.5 kcal/mol, consistent with the results of both Colket (9) and Hidaka et al. (19).

DISCUSSION

A mechanism for the above molecular dissociation channels is suggested by recognizing the vinylacetylene as a substituted ethylene, which like ethylene has no weak bonds. The primary dissociation channel in C_2H_4 is now known to be H_2 elimination (27,28). This evidently involves a 1,1-elimination to singlet vinylidene ($:C=CH_2$) (29) which very rapidly isomerizes to C_2H_2 (30). We now propose that C_4H_4 dissociates analogously – by 2,2-elimination of C_2H_2

$$C_4H_4 \rightarrow :C=CH_2 + C_2H_2$$
$$\text{fast} \searrow \qquad\qquad\qquad 3)$$
$$\longrightarrow C_2H_2$$

or 1,1-elimination of H_2
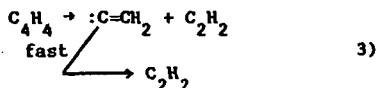
$$C_4H_4 \rightarrow :C=CH-C\equiv CH + H_2$$
$$\text{fast} \searrow \qquad\qquad\qquad 4)$$
$$\longrightarrow C_4H_2$$

We expect similar barriers for these two paths with a lower A-factor for separation of the much lighter H_2. This is then consistent with the predominance of product C_2H_2 and the near constancy of the C_2H_2/C_4H_2 ratios.

The latest value for the heat of formation of singlet vinylidene is 97.7 $\pm$ 2 kcal/mol, 43.5 kcal/mol above acetylene (31). Actually this is an upper limit and lower values have been proposed (32). The heat of reaction for C_4H_4 $\rightarrow :C = CH_2 + C_2H_2$ is then $\Delta H^o_{293} \leqslant 54.2 + 97.7-69 = 84.9$ kcal/mol, which would drop to below 83 kcal/mol at 0^oK. This reaction should have little reverse barrier, so 83 kcal/mol should exceed the forward barrier, and this is quite close enough to the 79.5 $\pm$ 3 kcal/mol obtained from the RRKM fit to the LS data.

By detailed balance, observation of the unimolecular dissociation of vinylacetylene to two acetylenes, reaction 3), establishes that a direct dimerization of acetylene to vinylacetylene does indeed occur. The only remaining phenomenological question is whether this can account for the entire second-order rate seen in C_2H_2 pyrolysis. We have calculated equilibrium constants for 3), and second-order rate constants for its reverse, using the k_∞ obtained from the RRKM calculations (this choice is discussed below). The result is compared to a schematic summary of the C_2H_2 dimerization data in Figure 6. Here the agreement with the (homogeneous) shock-tube data (4,6,9,12,17) and with the results of Palmer and Dormish (7) (which were corrected for heterogeneous reaction) is very good. The low temperature data (<1000K) may well have other problems besides heterogeneous reaction (see below), but this detailed balance calculation is anyway much too sensitive to the heat of formation of C_4H_4 at such low temperatures. A reduction of just 2 kcal/mol in this estimated ΔH^o_f will actually produce an excellent fit throughout. In any case it is clear that simple dimerization to C_4H_4 is a major part of what goes on in C_2H_2 pyrolysis.

The detailed mechanism of the C_2H_2 dimerization would now be isomerization to vinylidene followed by insertion of this into the C-H bond of acetylene (33)

$$C_2H_2 \rightarrow \; :C=CH_2 \qquad\qquad 5)$$
$$:C=CH_2 + C_2H_2 \rightarrow C_4H_4 \qquad 6)$$
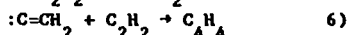
As long as 5) is equilibrated, the overall forward and reverse rates are still related by the equilibrium constant for 3). However, it is perfectly possible for 5) to be slow enough at low temperatures to generate a detectable induction period.

Although the calculated rates of dimerization to C_4H_4 in Figure 6 seem to account for the entire second-order rate above 1000K, this is rather misleading. Additional reaction paths are probably still necessary at both ends of the temperature range, i.e., outside 1000-1500K. For T>1500K the RRKM calculations show noticeable falloff even for the high pressures (3-10 atm) of the reflected shock experiments in Figure 6 (4,6,12). The use of k_∞ in the detailed balance calculation is then no longer valid, and the rates will begin to fall below the measured second-order data. However, consideration of the following reaction-enthalpy diagram
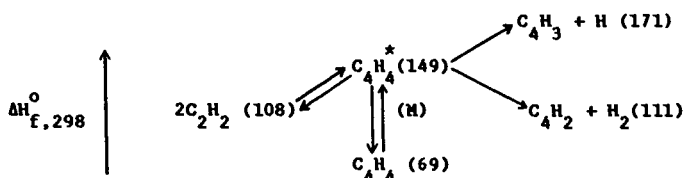
shows that when deactivation to C_4H_4 slows at high temperature (and/or low pressure) it opens the channels

$$2C_2H_2 \rightarrow C_4H_2 + H_2 \qquad\qquad 7)$$
$$2C_2H_2 \rightarrow C_4H_3 + H \qquad\qquad 8)$$
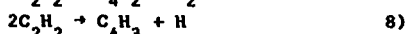
These will now act to "pull" the dimerization forward, at least partially compensating for the falloff in C_4H_4 formation. The chain initiated by 8) can also convert both C_2H_2 and any residual C_4H_4 to C_4H_2 and higher polyacetylenes, particularly at very high temperatures. Note that here neither 7) nor 8) can proceed till there is falloff of the deactivation, i.e., above about 1500K. The onset of these two channels may provide a reasonable explanation for the crossover from C_4H_4 to C_4H_2 in C_2H_2 pyrolysis which occurs around 1500-1600K (6,7,9). However, a quantitative modeling on this basis may be quite difficult below 1600K, where production of H-atom through reaction 8) must be very slow and could be overwhelmed by impurity generation. We would also suggest the isotopic scrambling in C_2H_2/C_2D_2 mixtures (6), alluded to earlier, probably requires very little H-atom (34) which could be generated by a small contribution from 8) and/or various impurities.

Below 1000K the situation may be even more complex. The pyrolysis now involves polymer, tar, and char formation and has a significant heterogeneous component (5,7,11). Minor products which suggest chain reaction may be generated by polymer carbonization, heterogeneous reaction, or for that matter, impurity initiated chain reaction.

Finally, we offer a highly tentative explanation for the polymer formed at the lowest temperatures. Usually carbenes preferentially insert into multiple bonds (33), so the dominant insertion product should be methylenecyclopropene. This has now been synthesized (35,36) and is quite unstable. For one thing it evidently polymerizes (36); at high temperatures it probably reverts to C_2H_2. This suggestion is closely analogous to the triplet diradical schemes (5, 7, 18) and can deal with the same phenomena. In addition to the right energetics, it also has the advantage of fading out at high temperatures where the methylenecyclopropene reverts to acetylene.

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